Coherency Strain as an Athermal Strengthening Mechanism

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(Received 6 January 1997)

We have grown homogeneous thick layers of InGaAs on InP with 0.2% strain and also coherently strained superlattices with the same net strain. The thick layers can relax by plastic deformation during growth, and relax further under annealing at higher temperatures. In contrast, superlattices with alternating coherency strains remain fully strained even under annealing at 900 °C, above 85% of their estimated melting points. We conclude that coherency strain can be a powerful strengthening mechanism which is athermal and hence useful for high-temperature structural materials. [S0031-9007(97)03220-1]

PACS numbers: 68.65.+g, 62.20.Fe, 81.40.Lm

There has long been an awareness that coherency strain may act as a strengthening mechanism in materials [1]. Cahn, for example, suggested in 1963 that alternating coherency strains due to spinodal decomposition played a part in the hardening of many important age-hardening alloys such as Inconel and the Nimonics, and gave a theoretical account of how dislocation movement could be obstructed by the coherency strain field [2]. However, experimental verification of these ideas has been lacking. Part of the difficulty is that coherency strain is not easy to control or to characterize in most structural materials. In semiconductors, pseudomorphic epitaxial crystal growth techniques enable high coherency strains to be produced with good control, and high resolution x-ray diffraction enables the strain to be measured accurately. Here we use these techniques to demonstrate that coherency strain in a semiconductor superlattice is indeed a strengthening mechanism and that it is operative to very high fractions of the melting point.

Superlattice structures were made of strained $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloys grown epitaxially on single crystal S-doped InP substrates with a dislocation density of $10^2-10^3\ \mathrm{cm}^{-2}$. The lattice constant a_0 of InP is 5.8687 Å (at 300 K), while that of $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$ depends on x and is given by Vegard's Law, by linear interpolation between the binary compounds, $a(x) = (5.6533 + 0.4050x)$ Å [3]. Consequently, an alloy grown epitaxially on InP with the composition $x = 0.53$ is lattice matched and unstrained, while lower values of x result in tensile coherency strain and higher values in compressive strain. Differences in thermal expansion coefficients are small, so we neglect the effect of temperature on coherency strain. We grew superlattices consisting of twenty-four repeats of a pair of 50 nm (nominal) layers of alternate 0.4% tensile and 0.8% compressive strain (Fig. 1). The total nominal thickness of the structures was thus 2.4 μm. With the compressive strain 0.4% higher than the tensile in absolute magnitude, the superlattices were under 0.2% net compressive strain. We also grew superlattices of the same design but with the difference in the strains between adjacent layers progressively reduced so that the individual layer strains were closer to the net strain, finishing with homogeneous layers with 0.2% compressive strain throughout (Table I). The structures were grown using molecular beam epitaxy

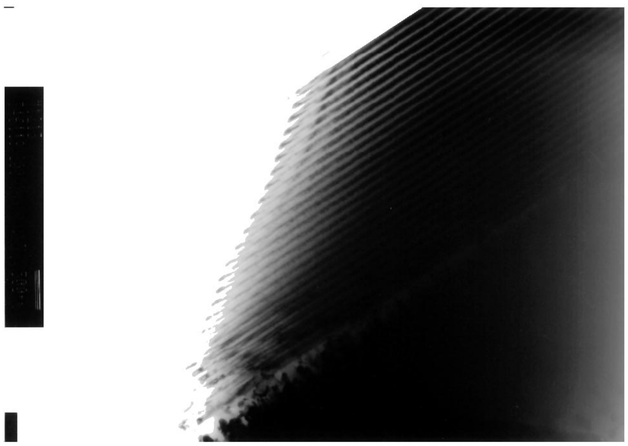

FIG. 1. The +0.8%/−0.4% superlattice is shown in cross section by transmission electron microscopy. The layers are seen to be flat and close to nominal thickness (50 ± 2 nm from this image, 50 ± 1 nm from the x-ray data of Fig. 2).

TABLE I. Sample design parameters, measured misfits, and measured strains (in percent).[a]

Sample	2.5 μm layer	2.5 μm layer	Superlattice	Superlattice	Superlattice	Superlattice
Nominal misfit	+0.2	+0.2	+0.3, +0.1	+0.4, 0	+0.6, −0.2	+0.8, −0.4
Actual misfit	+0.26	+0.18	+0.32, +0.06	+0.42, +0.01	+0.58, −0.25	+0.84, −0.35
Strain as grown	+0.21	+0.18	+0.32, +0.06	+0.42, +0.01	+0.58, −0.25	+0.84, −0.35
10 min at 600 °C	+0.16	⋯	broadened	⋯	⋯	⋯
135 s at 700 °C	+0.14	⋯	broadened	⋯	⋯	⋯
45 s at 800 °C	+0.11	⋯	very broad	⋯	⋯	⋯
15 s at 900 °C	+0.10	⋯	very broad	⋯	⋯	⋯
30 s at 900 °C	⋯	+0.09	uninterpretable	+0.37, −0.04	+0.58, −0.25	+0.84, −0.35

[a] Note that compressive strains are given a positive sign for consistency with misfit.

at 450 °C; this rather low temperature was found to be necessary to inhibit wavy layer growth and keep the interfaces flat, as seen in Fig. 1.

High-resolution x-ray analysis was carried out using a double-crystal diffractometer. The as-grown superlattices gave rocking curves characteristic of pseudomorphic growth, with well-resolved peaks due to the superlattice periodicity [Figs 2(b),2(f)]. Comparison with simulations generated by RADS software [4] [Fig. 2(a), 2(e)] enabled the thicknesses of the layers to be verified, and the compositions and strains to be deduced (Table I). The homogeneous layers were slightly relaxed, and their rocking curves were analyzed for composition and strain by the traditional techniques [5,6].

Samples were annealed above their growth temperature of 450 °C. A rapid thermal annealing graphite-strip furnace was used, with proximity capping to reduce arsenic desorption from the layers. This was done by placing two 6 mm × 6 mm samples of the same structure together, epitaxial faces in contact. Proximity capping is not as effective as a dielectric cap such as silicon nitride, but was chosen to avoid additional and unknown stresses on the layers from a cap. The annealing times at high temperatures were chosen to fall within the limits of proximity capping. On annealing at progressively higher temperatures, the homogeneous layers relaxed further while the superlattices initially remained pseudomorphic. At the higher temperatures, the superlattices with only compressively strained and unstrained layers showed degraded rocking curves, with a loss of resolution of the fine structure [Fig. 2(d)] characteristic of the presence of dislocations. At 900 °C, the peaks shifted, showing that plastic relaxation occurred [Fig. 2(d)]; the extent of relaxation was found by comparison with simulations [Fig. 2(c)]. In contrast, the superlattices with strains of alternating sign showed no evidence of degradation or relaxation even at the highest temperatures: In Fig. 2 we see that the rocking curves for the sample as grown [Fig. 2(f)] and annealed at 900 °C [Fig. 2(g)] are very similar and well fitted by the simulated curve [Fig. 2(e)] for the as-grown structure.

This is an encouraging result. All these structures have a total thickness very much greater than the equilibrium critical thickness of about 50 nm for the introduction of misfit dislocations into layers of 0.2% strain [7]. They are also much thicker than the relaxation critical thickness of about 400 nm at which significant plastic relaxation is expected from previous experiments [8,9]. All the structures are therefore expected to relax towards the theoretical residual net strain value of 3×10^{-4} [10]. The homogeneous layers do so, which indicates that the nucleation of dislocations is possible (unrelaxed SiGe layers much thicker than critical thickness have frequently been reported, but it is the very high perfection of silicon-based crystals which is thought to make nucleation of dislocations unlikely [11]). The superlattices with only compressive, or compressive and unstrained, layers show some increased strength, perhaps due to the interfaces.

The dramatic difference in the behavior of the alternately strained superlattices is in accordance with our earlier predictions [10,12,13]. Beanland explained the difference between equilibrium critical thickness and relaxation critical thickness in terms of the inability of dislocation sources, such as the spiral source or the Frank-Read source, to operate in a layer less than a few times thicker than equilibrium critical thickness [14]. Each individual layer in the alternately strained superlattices is below relaxation critical thickness (100 nm for the 0.8% layers [8]), and so a Frank-Read source cannot operate within a single layer under the influence of the coherency stress. The tensile layers prevent a source from operating across two or more layers, since the dislocation loop would have to cross the tensile layer *against* the tensile strain field. In principle, it would seem the alternately strained superlattice could be made indefinitely thick and so form the basis of a designed lamellar material with high strength at high temperature. Furthermore, the plasticity could be controlled by the designer, since an applied external tensile strain field sufficient to bring the tensile layers to zero strain enables plastic deformation to occur. Nothing in our interpretation depends on the material system—we chose III-V semiconductors for convenience—and these arguments should apply as well to metals and ceramics if they can be grown with the same control as semiconductors.

The stability of the alternately strained superlattices in the wide temperature range investigated is indicative of the inability of dislocation sources to operate, whether

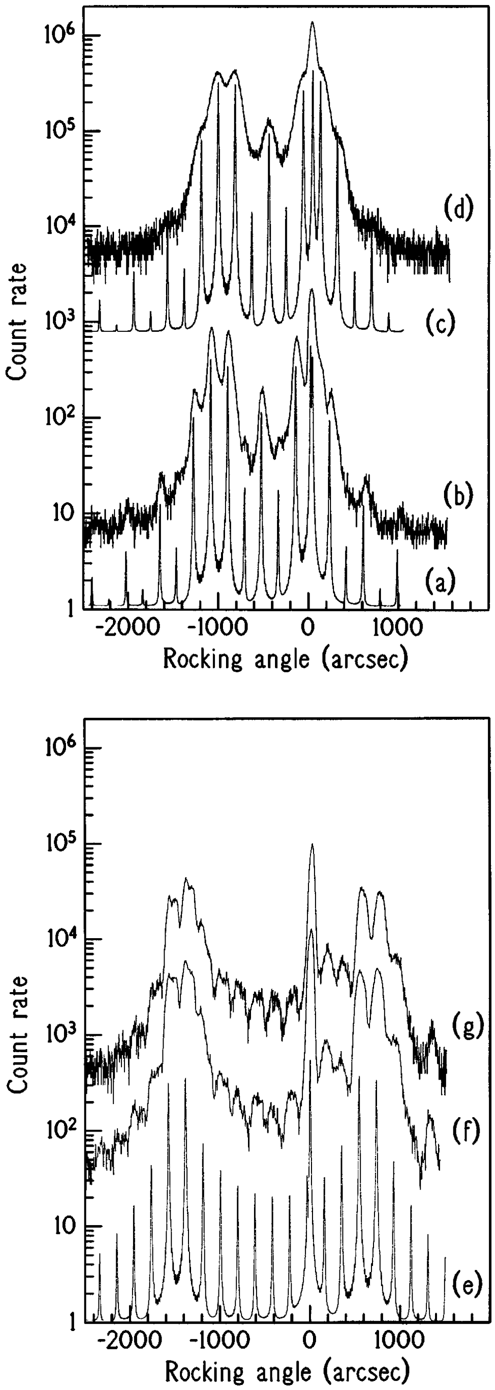

FIG. 2. Double-crystal x-ray rocking curves and simulations are shown for the $+0.4\%/0\%$ [(a)–(d)] and the $+0.6\%/-0.2\%$ [(e)–(g)] superlattices (the curves are shifted vertically for clarity). Curves (b) and (d) are the experimental curve for the $0.4\%/0\%$ sample as grown and after annealing, and (a) and (c) are the simulations from which its strains are established. Comparison of curves (c) and (d) with (a) and (b) shows a clear shift of the peaks which corresponds to a change of strain of 0.05%. The fringe structure is less well resolved in (d), corresponding to the presence of some dislocations. In contrast, the experimental curves for the $+0.6\%/-0.2\%$ superlattice as grown (f) and annealed (g) are identical and fitted by the same simulation (e), showing that no relaxation or degradation has occurred.

by glide or climb. The samples are single crystals, with no second phases or grain boundaries and no obvious obstacle to dislocation movement or multiplication other than the varying coherency stresses. We conclude that we observe a real strengthening mechanism. The melting point of InGaAs lattice matched to InP ($x = 0.53$) does not appear to be known [3]; linear interpolation between the melting point of GaAs (1513 K) and InAs (1215 K) gives 1355 K for $x = 0.53$ and 1325 K for the 0.8% strained layers. The coherency strain strengthening, still operative at 900 °C, is thus demonstrated to be athermal up to a very high fraction near nine-tenths of the estimated melting point.

We are grateful to the Engineering and Physical Sciences Research Council (U. K.) for financial support

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